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# SIMPLE DESALINATION PROCESS FOR MAKING AGRICULTURAL CULTIVATION SOLUTION FROM SEAWATER USING NATURAL ZEOLITE AND ACTIVATED ALUMINA

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## Abstract

*We attempted to make agricultural cultivation solution from seawater with a two-step process using natural zeolite and activated alumina. Natural zeolite used in this study is Japanese mordenite-type zeolite with high content of $Ca^{2+}$ as exchangeable cation. Activated alumina can remove anions, $SO_4^{2-}$ and $Cl^-$, and divalent cations, $Mg^{2+}$ and $Ca^{2+}$, better than monovalent cations, $Na^+$ and $K^+$, from seawater. By treating seawater with natural zeolite, the obtained solution contains higher divalent cations and lower monovalent cations than seawater, due to the ion exchange of natural zeolite, and removal of cations from the obtained solution is higher than that from seawater using activated alumina, while removal of anions is almost same. Radish sprouts can be grown in the solution after two-step treatment of natural zeolite and activated alumina, while they cannot be grown in seawater and the solutions after one-step treatment of natural zeolite and activated alumina.*

**Keywords**

Agricultural Cultivation Solution, Seawater, Natural Zeolite, Activated Alumina, Radish Sprouts

## 1. Introduction

Stable supply of food is essential to sustain human life. Agricultural water is one of the most important factors in food production. Recent environmental problems (e.g. soil desertification) are major contributors to water resources decline for agriculture. During the twentieth century, the global human population increased fourfold, but the water from natural freshwater resources we need increased eightfold (Abdul, 2006).

Effective resources utilization is an important issue for the twenty-first century (WWC, 2002), and seawater desalination is one of the ways to supply water. Well-known desalination technologies worldwide are the multi-stage flash (MSF) method and reverse osmosis membrane method (RO) (Semiat & Hasson, 2012; Szytel, 2005). In these technologies, almost all ions contained in seawater are removed, leaving fresh, high-quality water for domestic or industrial use. For the most common use for water worldwide, 70% of the total use of freshwater is for irrigation (Tilzer, 2006). Water made by MSF or RO for agriculture is expensive, and high-purity water requires the addition of fertilizer for agricultural use because water used for agriculture should contain nutrients, such as $K^+$, $Mg^{2+}$, $PO_4^{3-}$ and $NO_3^-$, to some extent. Seawater contains the essential elements needed for plant growth, but the high concentration of NaCl causes salt damage for direct use of agriculture. Producing irrigation water from seawater by reducing NaCl using a simple process would therefore be very beneficial.

In this study, a new simple process to reduce the NaCl concentration in seawater using natural zeolite and activated alumina was attempted. Natural zeolite is usually associated with grassy volcanic rock in natural deposits, and is available in large quantities at low cost (Barrer, 1978). Based on their high ion-exchange capacity, absorptivity, water retention and low cost, natural zeolites have been used in agronomy, horticulture and industry (DNUM, 1994). Natural zeolite can therefore be used to reduce $Na^+$ in seawater by ion exchange at low cost (Wajima, 2013). There are some reports for the $Na^+$ reduction in soil (Noori, Zendehdel, & Ahmadi, 2006; Noori, Ahmadi, & Zendehdel, 2007), compost (Turan, 2008), or natural gas co-produced water (Zhao, Vance, Ganjegunte, & Urynowicz, 2008; Zhao, Vance, Urynowicz, & Gregory, 2009), using natural zeolite.

The combination process of natural zeolite with activated alumina treatment was examined, and then applied the prepared solution for radish sprouts growth. Activated alumina is a high-surface-area, highly porous form of aluminum oxide, and is capable of removing a variety of substances, for examples, harmful anions, such as fluoride, arsenic and selenium, by adsorption on the surface of the activated alumina. Radish sprout is a salt-sensitive crop, and the prepared solution could apply to many other vegetables when the solution can apply to radish sprouts growth (Shannon & Grieve, 1999). The possibility of the solution prepared from seawater using this process for agricultural cultivation was examined.

## 2. Experimental

### 2.1 Sample

Seawater was collected from the surface layer in Imari Bay, Saga Prefecture, Japan. Natural zeolite used in this study, a mordenite-type zeolite obtained from the deposit of Iizaka in Fukushima prefecture, Japan, has 1.67 mmol/g of cation exchange capacity, and contains $Na^+$ (0.56 mmol/g), $K^+$ (0.21 mmol/g), $Mg^{2+}$ (0.03 mmol/g) and $Ca^{2+}$ (0.44 mmol/g) as exchangeable cations (Wajima, 2013). Natural zeolite was grounded by a mill, particles less than 500 µm were sorted, and heated at 60 $^oC$ overnight before zeolite treatment. Commercially available activated alumina (Merck KGaA) was used in activated alumina treatment.

### 2.2 Seawater Treatment

Two treatments using natural zeolite and activated alumina were carried out (Fig. 1).

For natural zeolite treatment, 20 g of natural zeolite was added to 200 mL of seawater, and the slurry stirred for 2 h with a magnetic stirrer. After stirring, the solution was filtered, and 20 g of fresh natural zeolite was again added to the filtrate, and then stirred for 2 h. This process was repeated 10 times to obtain the solution treated with natural zeolite (NZ-solution).

For activated alumina treatment, 20 g of activated alumina was added to 200 mL of seawater or NZ-solution, and the slurry stirred for 2 h with a magnetic stirrer. After stirring, the solution was filtered, and 20 g of fresh activated alumina was again added to the filtrate, and then stirred for 2 h. This process was repeated 7 times to obtain the solution treated with activated alumina (AA-solution) and the solution treated with natural zeolite and activated alumina (NZ-AA-solution). The pH of the filtrate on each number of activated alumina treatment was measured with a pH meter (MA-130; Mettler, Toledo, OH, USA) and the concentrations of $Na^+$,

$K^{+}$, $Mg^{2+}$, $Ca^{2+}$, $Cl^{-}$ and $SO_4^{2-}$ in the solution on each number of activated alumina treatment were determined using ion chromatography (DX-120, Dionex, Japan) to calculate the removal of each element from sweater ($R$ (%)) as follows;

$$R = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

where $C_0$ is the initial concentrations of each element in seawater (mg/L), and $C$ is the measured concentrations of each element in the solution after treatment (mg/L).

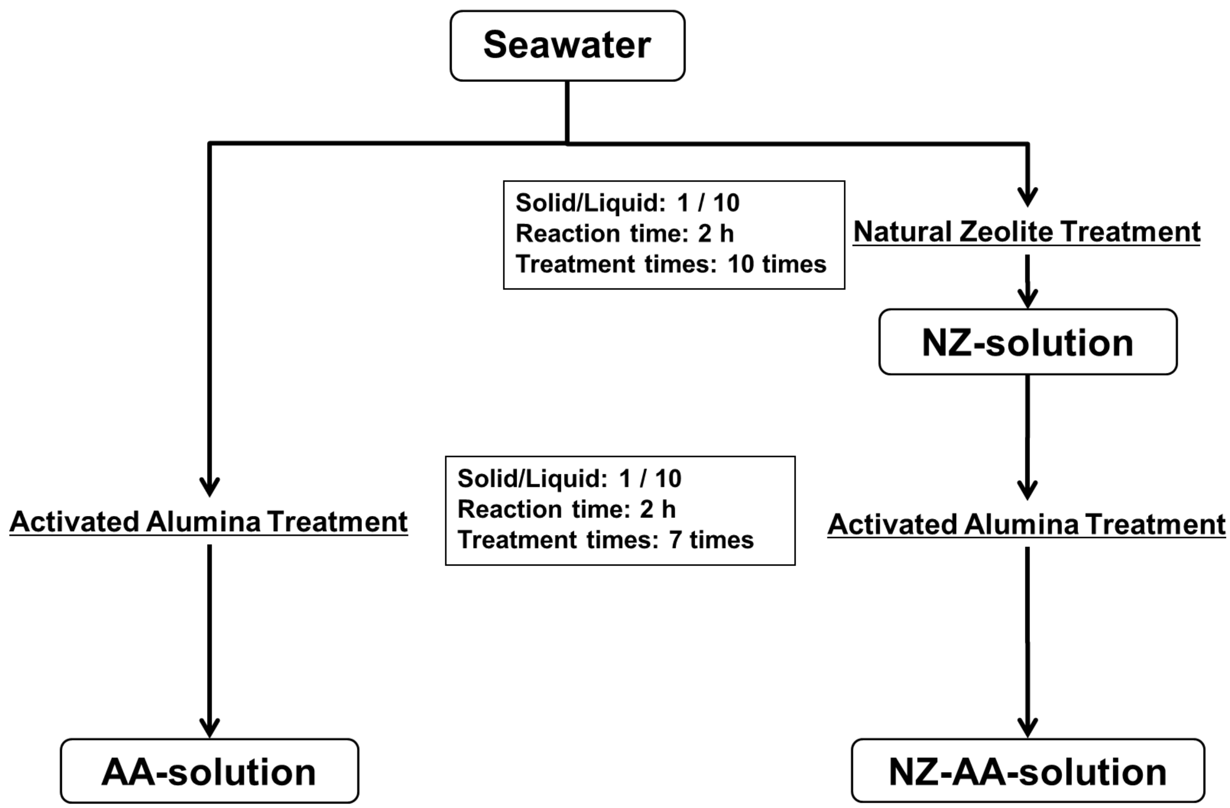


**Figure 1:** *Experimental procedure for desalination test from seawater using natural zeolite and activated alumina.*

### 2.3 Radish Sprouts Growth

Radish sprouts (Raphanus sativus) was grown for 10 days at 25°C using the cultivation solution obtained from each process.

## 3. Results and Discussion

Figure 2 shows the removal behaviors of main elements in seawater, $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$, from (a) seawater and (b) NZ-solution using activated alumina. In both seawater and NZ-solution, anions, $Cl^-$ and $SO_4^{2-}$, can be removed using activated alumina, and the removal of divalent anion, $SO_4^{2-}$, is more effective than that of monovalent anion, $Cl^-$. For cation removals, the removals of divalent cations, $Mg^{2+}$ and $Ca^{2+}$, is more effective than those of monovalent cations, $Na^+$ and $K^+$, and the order of effective removal using activated alumina is $Mg^{2+} > Ca^{2+} > K^+ > Na^+$.

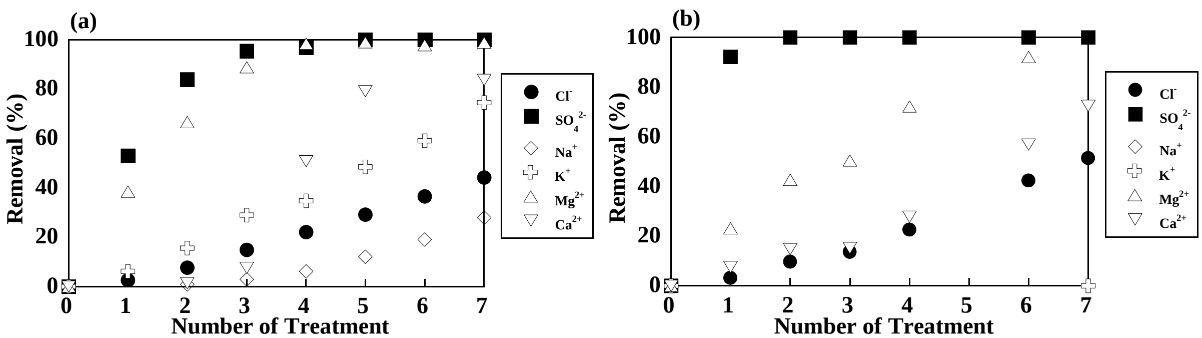


**Figure 2:** *Removal Behaviors of Main Elements in Seawater from (a) Seawater and (b) NZ-Solution using Activated Alumina*

Table 1 shows the chemical compositions and pH of seawater, NZ-solution, AA-solution and NZ-AA-solution. Seawater contained the high concentrations of both $Na^+$ and $Cl^-$, at 10272 mg/L and 19589 mg/L, respectively, and pH is 7.43. In NZ-solution, pH of the solution becomes 4.98 because mordenite is acidic mineral, monovalent cations, $Na^+$ and $K^+$, decreased, and $Mg^{2+}$ and $Ca^{2+}$ increased because of ion exchange between the $Mg^{2+}$ and $Ca^{2+}$ in natural zeolite and the $Na^+$ and $K^+$ in seawater. Anions, $Cl^-$ and $SO_4^{2-}$, in NZ-solution are slightly lower than those in seawater. Using activated alumina, the concentrations of $Cl^-$ and $SO_4^{2-}$ in AA-solution are about half of that in seawater (10934 mg/L) and zero, respectively, and pH of the solution is 6.43. $K^+$, $Mg^{2+}$ and $Ca^{2+}$ were also found to greatly decrease, while $Na^+$ slightly decreases. By the combination of natural zeolite and activated alumina, anions can be greatly reduced, and $Na^+$ in NZ-AA-solution is about one-fifth of that in seawater, while high contents of $Mg^{2+}$ and $Ca^{2+}$ remains in NZ-AA-solution (1218 mg/L and 1218 mg/L, respectively). It is noted that pH of NZ-AA-solution is neutral (6.48). Therefore, it is considered that desalination of NZ-solution using activated alumina is better than that of seawater directly, because zeolite treatment can exchange monovalent cations to divalent cations in seawater by ion exchange.

**Table 1:** *Chemical composition and pH of seawater, NZ-solution, AA-solution and NZ-AA-solution*

| | Chemical composition (mg/L) | | | | | | pH |
|---|---|---|---|---|---|---|---|
| | $Na^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Cl^-$ | $SO_4^{2-}$ | |
| Seawater | 10272 | 340 | 1277 | 312 | 19589 | 2479 | 7.43 |
| NZ-solution | 2020 | 56 | 832 | 4421 | 17058 | 1683 | 4.98 |
| AA-solution | 7406 | 86 | 14 | 51 | 10934 | 0 | 6.74 |
| NZ-AA-solution | 3159 | 0 | 38 | 1218 | 8294 | 0 | 6.48 |

Radish sprouts were experimentally cultivated with seawater, NZ-solution, AA-solution and NZ-AA-solution. Figure 3 shows the pictures when Radish sprouts is grown with each solutions for 10 days at 25 °C. We could confirm that Radish sprouts could cultivate in NZ-AA-solution through a two-step process (Fig. 3 (d)), although it could not cultivate in the seawater, NZ-solution and AA-solution (Fig. 3 (a), (b), (c)) due to the high contents of $Na^+$ and $Cl^-$. It is confirmed that the solution prepared from seawater using this process can be used for a cultivation solution.

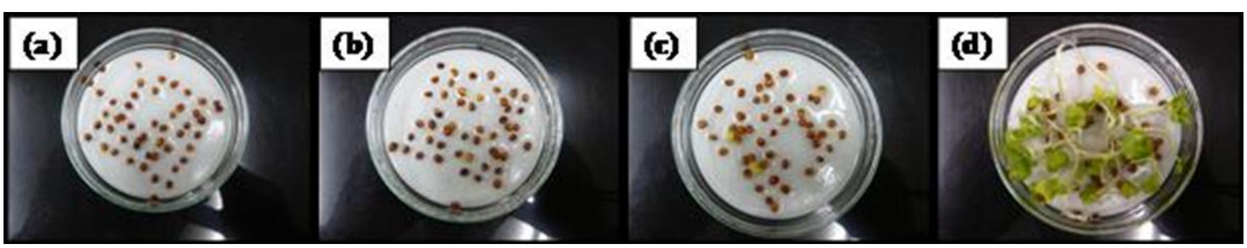


**Figure 3:** *Observation of Radish Sprouts after Ten-Days Growing using (a) Seawater (b) NZ-Solution, (c) AA-Solution and (d) NZ-AA-Solution*

## 4. Conclusion

We attempted to make a solution for agricultural cultivation from seawater with a two-step process using natural zeolite and activated alumina. We could decrease $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$ in seawater using activated alumina, and decrease $Na^+$ by ion exchange using natural zeolite. The NZ-AA-solution obtained by two-step process was neutral, and includes the nutrients, $Mg^{2+}$, and $Ca^{2+}$, and low levels of $Na^+$, $K^+$, Cl- and $SO_4^{2-}$, which is possible to use for cultivation. Radish sprouts can be grown in NZ-AA-solution, while those did not grow in seawater, NZ-solution and AA-solution, due to the high content of $Na^+$ and $Cl^-$. These results suggest that it is possible to prepare agricultural cultivation water from seawater using activated alumina by combination with natural zeolite. In future, we will try to prepare the desalination agent using natural zeolite and activated alumina to desalinate high saline water to use for agriculture.

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